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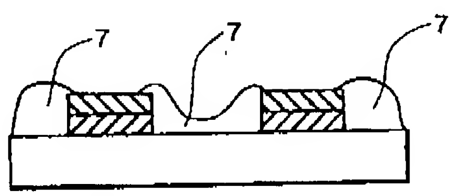
(54) Method for making thick film/solder joints.

(57) A method for making a thick film/solder joint comprising the sequential steps of:
(1) applying a layer of first thick film conductor paste to an electrically non-conductive substrate in a pattern which has preselected solder pad areas and firing the layer;
(2) applying over the first thick film layer only within the solder pad area a layer of a second thick film conductor paste having a low frit content and firing the layer; and
(3) forming the solder joint by applying to the fired second thick film layer a layer of soft solder.

Fig. 5e



Fig, 5f

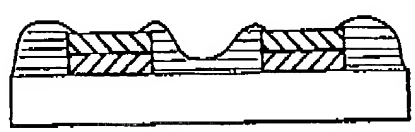
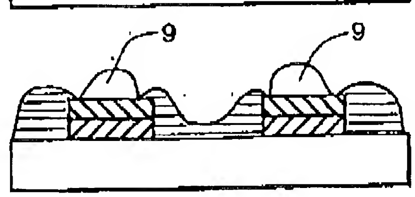


Fig. 5g



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Field of the Invention

The invention is directed to a method for making thick film/solder joints and, in particular. it is directed to such a method which will produce thick film/solder joints which have good thermal cycled adhesion.

Background of the Invention

The current trend in the microelectronics industry is to surface mount integrated circuits and other components onto thick film metallized substrates. Although this is a cost effective interconnection and packaging method which lends itself to mass production, certain reliability problems have been encountered in trying to implement its approach. Soldering, which is the preferred method for attaching leads and IC packages, can lead to solder joint failures-particularly on thermal cycling. This has severely limited the use of thick films for certain applications such as automotive electronics and sonic military and high power applications where good thermal cycled performance is essential.

The engine compartment of an automobile is a particularly severe environment where circuits encounter temperatures of 150C during normal operation and excursions to 160 to 170C for short times after the engine is stopped. Conversely, in some areas, the ambient temperature can drop to -50C. Although the above temperatures represent extreme conditions, the circuit must be able to withstand a significant number of thermal cycles in this temperatures range without appreciable degradation in adhesion to avoid catastrophic failure. This ability to withstand thermal cycling conditions, i.e., thermal cycled adhesion (TCA), is becoming even more important because of the longer warranty periods that are now being offered by automobile manufacturers.

Conventional Ag/Pd thick film conductors soldered with Sn/Pb eutectic solder exhibit relatively poor thermal cycled adhesion. Sn/Pb solders have a much higher thermal coefficient of expansion (TCE) than the alumina substrate and thick film conductor. This mismatch in TCE results in high tensile stresses in Sn/Pb solder joints made to thick film conductors.

Although surface mount technology (SMT) is an attractive assembly method for high density electronic systems, there are still problems which must be solved. LCC, MLC, and other chip components are generally attached to alumina or ceramic multilayer Interconnect boards via reflow of Sn/Pb solder paste. Since a large TCF mismatch exists between the substrate, metallization and solder, it is apparent that a tensile strain will be induced into the thick film at the base of the solder fillet. For the case of a soldered copper thick film on an alumina substrate, the strain ϵ due to the TCE mismatch can be estimated as follows:

For soldered Cu film thermally cycled between -50 and +150C

$$\epsilon = \Delta \alpha \cdot \Delta T$$
$$\epsilon = (25\text{-}6)(200) = 3800 \text{ ppm}$$

The tensile stress in the copper film, σ_{cu}, can be estimated from Hookes law:

$$\sigma_{cu} = \epsilon E$$

where E is Young's modulus of Elasticity

For thermal cycling between -50 and +150C, the tensile stress is estimated to be:

$$\sigma_{cu} = 3800 \times 10^{-6} \cdot 3\times10^{6} = 11{,}400 \text{ psi (tension).}$$

This calculation is only approximate because α_{cu} (thick film) is less than α_{cu} (bulk) and some of the tensile stress will be relieved by plastic flow in the solder and copper. More accurate estimates of stresses in SMT solder joints have been made by the Finite Element Method (FEM) of analysis. The FEM results indicate tensile stresses of the same order of magnitude. Obviously, the presence of an LCC or IC chip further complicates the stress situation.

The important point is that tensile stresses due to TCE mismatch are considerable and any cracks which develop and propagate in the thick film conductor, dielectric, or IC chips can result in open circuit failures.

In addition to stresses caused by large differences in TCE, thick film solder pads are subjected to a number of mechanical and chemical interactions on thermal cycling which degrade adhesion, namely:

- Tin diffusion from the solder into the film with the formation and growth of intermetallic compounds.

- Formation of a weak, Pb-rich zone in the solder.
- High strains due to the large TCE mismatch between solder fillet and film/substrate.
- Creep related processes including coalescence of microvoids and oxidation of the solder.
- Crack propagation through the solder/conductor to the substrate/dielectric interface.

Typical data for thermal cycled adhesion degradation of soldered thick film conductors are shown in Figure 1. All the curves exhibit a small initial drop in adhesion upon thermal cycling, followed by a rapid decline after extended cycling.

Summary of the Invention

In a first aspect, the Invention is directed to a method for making thick film/solder joints having a preselected area comprising the sequential steps of

(1) applying to an electrically non-conductive substrate a patterned layer having a preselected solder pad area of a first thick film conductive composition comprising finely divided particles of (a) 85.0-98.5% wt. of a pure unalloyed conductive metal or low alloy thereof selected from Au, Ag and Cu having a particle size of 0.5-5 microns, (b) 1-10% wt. glass frit, and (c) 0.5 to 5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;

(2) firing the first thick film conductive composition layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder;

(3) applying over only the solder pad area of the fired first thick film conductive layer a layer of second thick film conductor composition comprising (a) 94.0-99.3% wt. pure unalloyed conductive metal or low alloy of a metal selected from Au, Ag, and Cu having a particle size of 0.5-10 microns, (b) 0.2-1.0% wt. glass frit, and (c) 0.5-5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;

(4) firing the second thick film conductive layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder; and

(5) forming the solder joint by applying to the solder pad area of the fired second thick film conductive layer a layer of soft, low-Sn solder having a melting point of 120-300C.

In a second aspect, the invention is directed to a method for making a thick film/solder joint having a preselected area comprising the sequential steps of:

(1) applying to an electrically non-conductive substrate a patterned layer having a preselected solder pad area of a thick film conductive composition comprising finely divided particles of (a) 85.0-98.5% wt. of a pure unalloyed conductive metal or low alloy thereof selected from Au, Ag and Cu having a particle size of 0.5-5 microns, (b) 1-10% wt. glass frit, and (c) 0.5-5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;

(2) firing the thick film conductive composition layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder;

(3) applying over the exposed areas of the substrate circumscribing the solder pad area and to the outer edges of the thick film conductor within the solder pad area a thick film dielectric composition comprising finely divided particles of glass dispersed in organic medium;

(4) firing the thick film dielectric composition to effect volatilization of the organic medium therefrom and sintering of the glass therein; and

(5) forming the solder joint by applying to the surface of the thick film conductive composition which remains exposed on the solder pad area a layer of soft solder having a melting point of 120-300C.

Brief Description of the Drawing

The Drawing consists of six figures as follows:

Figure 1 is a graphical correlation of adhesion as a function of the number of thermal cycles for a variety of thick film materials;

Figure 2 is a graphical representation of three thermal cycle profiles which were used in the evaluation of the invention;

Figure 3 is a graphical correlation of adhesion as a function of aging time showing the effect of fired film thickness of the conductor;

Figure 4 is a graphic correlation of thick film conductor adhesion with aging at various temperatures;

Figure 5 is a schematic representation of the steps of the invention which are required to make a soldered thick film conductor element; and

Figure 6 is a drawing of the adhesion test bond configuration.

Figure 7 is a schematic cross sectional representation comparing the configurations of the standard and modified peel tests.

Detailed Description of the Invention

A. In General

The performance of thick film conductors subjected to thermal cycle tests can be improved by controlling several materials, process and design factors. For example, pure, ductile thick films with low glass binder content such as Ag or Cu exhibit higher thermal cycled adhesion than Ag/Pd alloy conductors. Likewise, thick, dense films exhibit greater thermal cycled adhesion than thin, porous films because it takes longer for tin diffusion from the solder to penetrate through the thick, dense film.

Solder composition and soldering conditions also play an important role. Thick films soldered with low yield strength, low-Sn or Sn-free solders perform better in thermal cycling because some stress relief occurs due to plastic deformation in the solder. Also, embrittlement of the thick film due to M_xSn_y intermetallic formation is reduced because of the lower tin content.

Sometimes on thermal cycling, fatigue failure of the solder joint occurs instead of failure at the thick film/substrate interface. This can be minimized by producing fine-grained, void-free solder joints and by employing solder compositions which have high fatigue strength. The Coffin-Manson equation is useful in comparing the fatigue strength of solders thermally cycled under various conditions.

$$N_f^a \cdot \Delta\varepsilon_p = \text{Constant}$$

Following is a list of factors which affect thermal cycled adhesion of thick film conductors. By controlling a combination of these factors, the performance of thick film materials on thermal cycling can be significantly improved.

B. Metallurgy

Thick film compositions of pure metals such as Ag, Cu, and Au or low alloys of these metals perform better on thermal cycling than hard, brittle alloys like 30/70 Pd/Ag. Pure metals and their low alloys are softer (low modulus) and therefore can relieve thermal cycling stresses by plastic flow. Furthermore, thick film Ag, Cu, and Au densify on firing without requiring large amounts of glass binder which makes the film brittle. Stress relief by plastic deformation inhibits crack propagation and results in higher thermal cycled adhesion.

As used herein, the term "low alloy" means that the primary conductive metal contains no more than 5% by weight of secondary alloying metal such as a 95/5 Ag/Pd alloy.

C. Fired Film Thickness

As shown by the data presented graphically in Figure 3, the use of thicker fired films improves aged adhesion. If sufficient thickness cannot be obtained in a single printing and firing operation, several conductor layers can be applied by sequential printing and firing or by cofiring two or more layers.

Standard thick film conductors are designed to have good solderability and adhesion when fired on 96% alumina substrates or over dielectric. When two layers of a conductor are built up by sequential firing, the top layer often will not have adequate solderability. This difficulty can be overcome by using a different composition for the top layer which contains less frit than the standard conductor designed for firing on ceramic. Therefore for optimum overall performance, multiple layer thick films may require different compositions for the bottom and top layers--particularly if the layers are sequentially fired rather than cofired.

In general, the first layer on the ceramic should be a thick film conductor with good TCA (dense, pure or low alloy metal film with mixed bonding) and the top layer should be a conductor with good aged adhesion (i.e., low frit and resistance to leaching and degradation by tin solders). Therefore a thick film conductor consisting of two layers of optimum composition will exhibit superior aged and thermal cycled adhesion to either single layer alone. More particularly, the first conductive thick film layer should contain 1-15% wt. mixed oxide/frit inorganic binder. At least 1% wt. inorganic binder is needed to get adequate

particle bonding. However, more than 15% wt. is likely adversely to affect TCA. On the other hand, the second lower frit conductive thick film layer should contain 0.7-6.0% wt. inorganic binder. At least 0.7% wt. inorganic binder is needed to get adequate bonding to the underlying thick film conductive layer, but more than 6.0% inorganic binder is likely adversely to affect solderability of the layer.

It should be mentioned that cofiring of more than one or two layers of Cu in nitrogen can lead to organic burnout problems and therefore is not preferred in the practice of the invention.

D. Composite/Gradient Thick Films

The above section discussed the benefits of using two or more layers of conductor of different composition but the same metallurgy, i.e., Ag or Cu or Au. Improved performance can result from using two different metallurgies, e.g., Ag and Cu and two different firing profiles.

For example, Du Pont 6160 Ag has excellent thermal cycled adhesion but poor solder leach and migration resistance and marginal long-term aged adhesion. By overprinting 6160 Ag fired in air at 850C with a Cu thick film paste (QS190) fired in nitrogen at 600C, a composite conductor is obtained which has the following advantages:

- High conductivity
- Excellent solderability
- Good solder leach resistance
- Resistance to migration
- High aged adhesion
- High thermal cycled adhesion
- Low cost

The overprint Cu must be fired in nitrogen below the Ag-Cu eutectic temperature of 780C to avoid melting. However, the composite Ag-Cu thick film exhibits a combination of properties which cannot be achieved from Ag or Cu alone.

E. Edge Encapsulation

In the course of the studies on which the invention is based, it has been found that both AA and TCA of the copper conductive layers can be enhanced by edge encapsulation. By "edge encapsulation", it is meant that a fired layer of dielectric composition is applied over the outer edges of the fired thick film conductor and the exposed areas of the substrate surrounding the solder pad.

Turning now to Figure 5 of the Drawing, it consists of seven figures (5a through 5g) which illustrate both the overprinting of thick film conductive layers and edge encapsulation to improve the AA and TCA of thick film conductive layers.

As shown in Figure 5a, a first thick film conductive layer 3 is applied by screen printing onto an alumina substrate 1. Upon completion of drying the paste, the layer 3 is fired at 800-950 °C to effect volatilization of the remaining organic medium in the paste and to sinter the inorganic binder (Figure 5b). A second layer of thick film conductive paste 5 is then printed over the fired layer 3 and dried (Figure 5c). After drying, the second thick film, conductive layer 5 is fired to effect volatilization of the organic medium in the paste and to sinter the inorganic binder (Figure 5d). A layer of dielectric thick film paste 7 is then applied over the exposed areas of the substrate 1 and the edges of the top fired conductive layer 5 (Figure 5e) and the dielectric layer 7 is fired to effect volatilization of the organic medium and sintering of the dielectric solids (Figure 5f). Soldering is then accomplished by applying molten solder 9 to the exposed areas of the top conductive layer 5 and cooling the solder to room temperature (Figure 5g).

F. Barrier Layers

Poor TCA performance is caused by high stresses due to TCE mismatch which are superimposed on the aging and interaction mechanisms as discussed hereinabove. These stresses can be reduced by using low modulus, high fatigue strength solders. Another approach is to use a barrier layer to inhibit solder/thick film interactions which degrade TCA.

The main purpose of the barrier layer is to prevent Sn diffusion into the film and the attendant formation of a weak, Pb-rich zone in the solder joint. Nickel is an effective diffusion barrier because Ni_xSn_y intermetallics grow at a very slow rate. However electroless and electrolytic processes must be carefully selected to prevent destruction of the glass/oxide thick film bond by acidic plating solutions.

0" depth at the other end. A blade is used to draw down paste along the length of the channel. Scratches will appear in the channel where the agglomerates' diameter is greater than the channel depth. A satisfactory dispersion will give a fourth scratch point of 10-18 typically. The point at which half of the channel is uncovered with a well dispersed paste is between 3 and 8 typically. Fourth scratch measurement of >20 µm and "half-channel" measurements of >10 µm indicate a poorly dispersed suspension.

The remaining 5% consisting of organic components of the paste is then added, and the resin content is adjusted to bring the viscosity when fully formulated to between 100 and 200 Pa.s at a shear rate of 4 sec^{-1}. The composition is then applied to a substrate, such as alumina ceramic, usually by the process of screen printing, to a wet thickness of about 30-80 microns, preferably 35-70 microns, and most preferably 40-50 microns. The electrode compositions of this invention can be printed onto the substrates either by using an automatic printer or a hand printer in the conventional manner, preferably automatic screen stencil techniques are employed using a 200-to 325-mesh screen. The printed pattern is then dried at below 200C, about 150C, for about 5-15 minutes before firing. Firing to effect sintering of both the inorganic binder and the finely divided particles of metal is preferably done in a well ventilated belt conveyor furnace with a temperature profile that will allow burnout of the organic matter at about 300-600C, a period of maximum temperature of about 700-1000C lasting about 5-15 minutes, followed by a controlled cooldown cycle to prevent over sintering, unwanted chemical reactions at intermediate temperatures or substrate fracture which can occur from too rapid cooldown. The overall firing procedure will preferably extend over a period of about 1 hour, with 20-25 minutes to reach the firing temperature, about 10 minutes at the firing temperature and about 20-25 minutes in cooldown. In some instances, total cycle times as short as 30 minutes can be used.

L. Test Procedures

Solderability: The solderability tests were performed as follows: The fired parts were dipped in a mildly active rosin flux such as Alpha 611, then heated for 3 seconds by dippping the edge of the ceramic chip in the molten solder. The chip was then submerged in the solder for 10 seconds, withdrawn, cleaned and inspected. Solderability was determined by the percentage of solder coverage (buildup) obtained on the thick film test pattern.

Adhesion: The adhesion was measured using an "Instron" pull tester in a 90° peel configuration at a pull rate of 2 inches per minute. Twenty gauge pre-tinned wires were attached to 80 mil x 80 mil pads by solder dipping for 10 seconds in 62 Sn/36 Pb/2 Ag solder at 220C or in 60 Sn/40 Pb solder at 230C using Alpha 611 flux. (Alpha 611 is a tradename for solder flux made by Alpha Metals Inc., Jersey City, NJ.) Aging studies were carried out in air in a Blue M Stabil-Therm® oven controlled at 150°C. After aging, test parts were allowed to equilibrate several hours in air before the wires were pulled. A peel force of at least 15 newtons after 1000 hours aging at 150°C. is considered to be essential for most applications.

The standard configuration of the Du Pont "peel" adhesion test is shown in Figure 6. The only difference in the modified peel test is that the thin edges of the thick film are encapsulated with a dielectric. Therefore, the full thickness of the conductor resists shear failure due to high tensile stresses at the base of the solder fillet, leading to improved TCA. Solder joint failures can be characterized as follows:

- Type A. Conductor/substrate interface failure (pad lift-off);
- Type B. Conductor/solder failure;
- Type C. Wire pull out from solder; and
- Type D. Substrate failure (divoting).

Thermal Cycled Adhesion (TCA): The TCA test employs the same adhesion (peel) test described in L above. However, instead of measuring adhesion after isothermal aging at 150C, the sample is tested after thermal cycling between two temperatures.

Thermal cycle test conditions such as ΔT, transition rate, film thickness, solder joint design, etc., must be carefully selected in order to accurately predict performance under actual service conditions. For example, extreme thermal shock conditions (large ΔT and transition time ≤ 2 minutes) can cause brittle fracture of the alumina substrate which may not accurately represent the type of failures observed under actual use conditions (e.g., automotive engine compartment). Likewise, cycling of soldered thick films through large ΔTs often results in failure due to fatigue cracking through the solder joint. Therefore the rate of transition and the temperature extremes on thermal cycling must be controlled to ensure that failure modes in accelerated tests are the same as those observed in the field. FEM analysis of stresses in various solder joint designs subjected to thermal cycling can be helpful in understanding observed failure modes under various processing and testing conditions.

Two types of thermal cycle equipment are generally used which differ in the transition rate between temperature extremes.

In single chamber equipment, the test assembly is placed in a single chamber and the heating and cooling cycles are carried out alternately in that chamber. In a dual chamber apparatus, one chamber is heated, the other is cooled, and the test assembly is transferred between them to obtain the temperature cycles. A suitable single chamber device is the VR CO8-PJ-3WG model made by Blue M Corporation, Blue Island, Illinois. A suitable dual chamber device is the model ATS-320 made by Thermonics, Santa Clara, CA.

The transition rate of the single chamber units is determined by the size of the refrigeration unit, thermal mass of the chamber plus load and the ΔT range. Figures 2a and 2b show typical thermal cycle profiles that were obtained with the Blue M equipment and used to generate the data given herein. Two standard ΔT profiles were used:

-40 to +125C (Figure 2a)

-50 to +150C (Figure 2b)

Because the Thermotron® dual-chamber unit consists of hot and cold chambers maintained at the desired temperature extremes and the test samples cycle rapidly between the hot and cold chambers, the transition rate between temperature extremes is much more rapid than in the single chamber equipment.

Figure 2c compares the "slow" vs. "fast" thermal cycle profiles obtained with the two types of equipment from -50 to +150C.

EXAMPLES

Examples 1-12

A number of thick film conductor compositions marketed by E. I. du Pont de Nemours and Co. were screen printed onto alumina and over Du Pont 5704 thick film glass dielectric. The dielectric was printed into layers and each layer was printed, dried and fired separately. All conductors were fired five times in air at 850C except 9922 Cu, which was fired at 900C in N_2. The thick film compositions are described in Table 1.

Table 1

Description of Thick Film Conductors		
Conductor	Binder	Composition -Ag/Pd Ratio
4093 Ag/Pd/Pt	Mixed	2.5/1 +4% Pt
4596 Au/Pt/Pd	Mixed	15% Pt/2.5% Pd
6125 Ag/Pd	Mixed	2.5/1
6134 Ag/Pd	Mixed	6/1
6160 Ag	Mixed	Ag
9476 Ag/Pd/Pt	Glass	1.8/1 +2% Pt
9922 Cu	Mixed	Cu
9924 Cu	Mixed (higher frit)	Cu
6001 Cu	Mixed (higher frit)	Cu
9153 Cu	Mixed - for firing at 900°C	Cu
9163 Cu	Mixed - for firing at 900°C	Cu
41062 Δ Cu	Mixed	Cu
41085 Δ Cu	Mixed	Cu
QS 170 Ag/Pt	Mixed	100 Ag/1 Pt
QS 180 Ag	Mixed	Ag

Each of the thick film pastes listed in Table 1 was printed on either alumina or Du Pont 5704 glass dielectric as described hereinabove and adhesion was measured after thermal cycling as indicated in Tables 2 and 3, which follow.

Table 2

Adhesion of Du Pont Thick Film Conductors After Thermal Cycling (-55 to +125C)										
Ex. No.	Conductor	Firing Cycle min.	Fired Thick µm	0	Average Adhesion (Newtons)Cycles				
					30	100	300	600	1000
1	6125 on alumina	30	14	30.7	16.4	12.0	7.6	7.2	3.6
2	6125 on 5704	30	14	28.9	17.8	8.0	3.1	2.2	0.9
3	6134 on alumina	30	14	27.6	14.2	8.4	9.8	6.6	0.9
4	6134 on 5704	30	13	28.9	12.0	6.6	3.3	3.1	4.4
5	6134 on alumina	60	14	31.1	10.2	7.1	3.6	3.2	1.3
6	6134 on 5704	60	14	30.2	9.3	2.7	3.6	1.8	0.9
7	4596 on alumina	60	15	32.0	16.9	11.1	8.0	5.0	1.5
8	4596 on 5704	60	12	28.0	16.9	6.7	3.6	2.7	2.2
9	9476 on alumina	60	13	30.7	9.3	2.7	0.4	0	0
10	4093 on alumina	60	15	29.8	20.0	16.9	5.8	0.9	1.3
11	6160 Ag on alumina	60	15	28.0	25.0	20.0	16.0	15.0	16.0
12	9922 Cu on alumina	60	14	30.0	28.0	20.0	14.0	14.0	12.0

Table 3

Adhesion of Du Pont Thick Film Conductors After Thermal Cycling (-40C to 125C in 1 Hour Cycle)							
Ex. No.	Conductor Composition	No. of Cycles				1000	
		100		500			
		Adhesion (Newtons)					
13	9922 Cu	26.0	(A)	11.8	(A)	0	(A)
14	9924* Cu	16.9	(A)	4.0	(A)	0	(A)
15	9153 Cu	25.2	(A)	14.9	(A)	7.4	(A)
16	9163 Cu	26.1	(A)	14.9	(A)	10.3	(A)
17	6001* Cu	17.5	(A)	8.4	(A)	5.1	(A)
18	4/062 Δ Cu	26.9	(B)	20.9	(B)	12.4	(A)
19	4/085 Δ Cu	28.1	(C)	27.7	(C)	15.8	(A)
20	QS170 Ag/Pt	36.4	(C)	18.7	(A)	0	(A)
21	QS180 Ag	35.9	(C)	23.2	(C)	10.68	(A)
22	6160 Ag	30.4	(C)	25.2	(C)	19.9	(A)
23	6134* Ag/Pd	14.0	(A)	6.0	(A)	0	(A)

*High frit containing thick film compositions
(A), (B), (C) denotes failure mode. (See Section L above.)
Δ - Experimental thick film pastes

The data in Table 3 show that high frit containing compositions, namely 9924 Cu, 6001 Cu and 6134 Ag/Pd have poor thermal cycle adhesion (TCA) performance compared to mixed-bonded, low-frit containing pure or low-alloy Ag and Cu compositions. From these data it is concluded that:

(1) Pure Ag and Cu thick films have higher TCA than Ag/Pd alloy conductors;
(2) Ag/Pd conductors show a significant loss in adhesion after only 100 cycles between -55 and 125C;
(3) Mixed bonded conductors generally have better adhesion than glass bonded conductors after thermal cycling; and
(4) The TCA of thick film conductors over dielectric is lower than over alumina.

Examples 24-40

Using the above described preparation and testing procedures, a series of 17 tests was performed to determine the effect of overprinting conductive layers on the Aged Adhesion (AA) and Thermocycle Adhesion (TCA) of copper thick films. In Examples 24-35, various copper thick film pastes were tested on alumina using both high and low tin solders. Both the top and bottom layers of the composite conductive layers were copper. Data from these tests are given in Table 4 below.

Table 4

Effect of Overprinting on Thermal Cycled Adhesion (TCA) of Copper Thick Films (-40 to +125°C)

Ex. No.	DuPont Copper	Solder Composition (Sn/Pb/Ag)	Adhesion in Newtons Ater Thermal Cycling							
			0		100		240		1000	
			C	P	C	P	C	P	C	P
24	6022	60/40	35	C	37	C	35	A	16	B
25		10/88/2	29	B	28	B	26	C	0	B
26	6022/9926	60/40	37	A	32	A	33	A	22	B
27		10/88/2	30	A	33	B	27	A	0	B
28	9161	60/40	29	A	31	B	31	B	0	A
29		10/88/2	23	B	24	B	19	B	0	B
30	9161/9926	60/40	26	A	27	A	34	A	21	B
31		10/88/2	22	A	26	A	24	A	11	A
32	9922	60/40	37	C	33	C	36	C	19	B
33		10/88/2	29	B	24	B	19	B	0	B
34	9922/9926	60/40	36	A	31	A	33	A	24	B
35		10/88/2	32	A	31	A	30	C	12	B

C = Cycles
P = Predominant Failure Mode

The data in Table 4 show potential improvements in the TCA after 1000 cycles of Cu conductors overprinted with low frit Cu paste. It can be seen, however, that the extent of the benefit of overprinting Cu on Cu also depends on solder type and binder composition. In general, ductile, low frit, thick film conductors exhibit better TCA but have poorer AA than high frit compositions. However, good AA and TCA can be obtained by overprinting a conductor with good TCA/poor AA with a conductor having Good AA/Poor TCA. This is shown in Table 5 for QS 175 AG overprinted with QS 191 (Example 39). However, poor TCA results when 6134 is overprinted with QS 191 (Example 40). Since 6134 and QS 191 have high glass content any cracks due to thermal cycling can propagate readily through the composite film causing failure. In the QS 175/QS 191 case, the ductile low frit QS 175 Ag layer stops the crack, thereby resulting in improved TCA performance. For this reason, composite films should be designed with a ductile, low frit mixed bonded first layer having good TCA overprinted by a second layer having good AA.

Table 5

Aged Adhesion (150°C) and Thermal Cycled Adhesion (-40 to +125°C) of Single vs. Composite Thick Films Conductors											
Ex. No.	Composite Conductor			Aged Adhesion Newtons-Hrs. at 150C				Therm.Cyc.Adhesion Newtons-No. of Cyc. -40 to +125°C.			
	Comp.	Bottom	Top	240	500	750	1000	240	500	750	1000
36	Cu	QS191	-	22	23	23	20	3	0	0	0
37	Ag	QS175	-	10	10	8	8	29	30	23	28
38	Ag-Pd	6134	-	32	31	30	30	26	19	7	5
39	Ag/Cu	QS175	QS191	31	25	25	27	32	30	29	27
40	Ag-Pd/Cu	6134	QS191	22	22	19	21	4	0	0	0

The data in Table 5 show that QS 191 Cu alone has good Aged Adhesion but very poor TCA. On the other hand, Ag alone exhibits rather poor Aged Adhesion but excellent TCA and Ag-Pd alloy exhibited very good aged adhesion, but rather poor TCA after 750 cycles. Nevertheless, when Cu was overprinted on Ag, excellent aged adhesion and TCA were both obtained.

Examples 40-43

A further series of four tests was conducted in the same manner to observe the effect of edge encapsulation as described hereinabove. In these tests, the overlap of the dielectric over the outer edges of the conductive layer was on the order of 250 microns in order to insure that no area of substrate was exposed due to misregistration of the patterns. However, 100-125 microns overlap is believed to be adequate provided there are no gaps due to misregistration.

Table 6 below summarizes adhesion peel test results after 500 and 880 cycles from -50 to +150°C. In the standard peel test design, the predominant failure mode is at the metal/dielectric interface (Type A). However, in the modified (edge encapsulated) peel test configuration, the observed failure mode is by fatigue cracking in the solder (Type B). Therefore edge encapsulation not only enhances thermal cycle performance but the failure mode is changed from the metallization to the solder. It is therefore apparent that the thermal cycle performance of these thick film compositions call be improved by using a different solder composition with a greater fatigue strength than 60 Sn/40 Pb solder and by changing the solder joint design (edge encapsulation).

Table 6

(Thermal Cycled Adhesion of 9153 Copper (-50 to +150°C) Standard vs. Modified Peel Test Configuration

Example No.	40	41	42	43
Copper	9153	9153	9153/ 9926	9153/ 9926
Peel Test Configuration	Std.	Mod.	Std.	Mod.
Dielectric	4575D	4575D	4575D	4575D
Solder	60/Sn/ 40 Pb	60/Sn/ 40 Pb	60/Sn/ 40 Pb	60/Sn/ 40 Pb
Flux	A-611	A-611	A-611	A-611
Temp. °C	230	230	230	230
Thermal Cycled Adhesion Newtons				
500 Cycles	15	26	19	32
PFM	A	C	A	C
880 Cycles	0	16	12	23
PFM	A	B	A	B

Claims

1. A method for making thick film/solder joints having a preselected area comprising the sequential steps of

(1) applying to an electrically-non-conductive substrate a patterned layer having a preselected solder pad area of a first thick film conductive composition comprising finely divided particles of (a) 85.0-98.5% wt. of a pure unalloyed ductile conductive metal or low alloy thereof having a particle size of 0.5-5 microns, (b) 1-10% wt. glass frit. and (c) 0.5 to 5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;

(2) firing the first thick film conductive composition layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder;

(3) applying over only the solder pad area of the fired first thick film conductive layer a layer of second thick film conductor composition comprising (a) 94.0-99.3% wt. pure unalloyed conductive metal or low alloy of a metal selected from Au, Ag, and Cu having a particle size of 0.5-10 microns, (b) 0.2-1.0% wt. glass frit, and (c) 0.5-5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;

(4) firing the second thick film conductive layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder; and

(5) forming the solder joint by applying to the solder pad area of the fired second thick film conductive layer a layer of soft solder having a melting point of 120-300C.

2. The method of claim 1 in which before step (5) a pattern of thick film dielectric composition comprising finely divided particles of glass dispersed in organic medium is applied to the exposed areas of the substrate circumscribing the solder pad area and to the outer edges of the thick film conductor within the solder pad area and the dielectric layer is fired to effect volatilization of the organic medium therefrom and liquid phase sintering of the glass.

3. The method of claim 1 in which the solder layer is applied by printing a thick film solder paste onto the solder pad area and drying the paste to remove the organic solvent therefrom.

4. The method of claim 1 in which the solder layer is applied by dipping the solder pad area in a molten solder ball, to form a solder coating thereon, removing the solder pad area from the molten solder bath and cooling the applied solder coating.

5. The method of claim 2 in which the glass in the thick film dielectric layer is crystallizable under the firing conditions.

6. The method of claim 1 or 2 in which the conductor metal or low alloy thereof in the first conductive layer is Ag and the conductive metal or low alloy thereof in the second conductive layer is Cu.

7. A method for making a thick film/solder joint having a preselected area comprising the sequential steps of:

(1) applying to an electrically non-conductive substrate a patterned layer having a preselected solder pad area of a thick film conductive composition comprising finely divided particles of (a) 85.0-98.5% wt. of a pure unalloyed conductive metal or low alloy thereof selected from Au, Ag and Cu having a particle size of 0.5-5 microns, (b) 1-10% wt. glass frit, and (c) 0.5-5.0% wt. spinel-forming metal oxide, all of (a), (b) and (c) being dispersed in organic medium;
(2) firing the thick film conductive composition layer to effect volatilization of the organic medium therefrom and liquid phase sintering of the inorganic binder;
(3) applying over the exposed areas of the substrate circumscribing the solder pad area and to the outer edges of the thick film conductor within the solder pad area a thick film dielectric composition comprising finely divided particles of glass dispersed in organic medium;
(4) firing the thick film dielectric composition to effect volatilization of the organic medium therefrom and sintering of the glass therein; and
(4) forming the solder joint by applying to the surface of the thick film conductive composition which remains exposed on the solder pad area a layer of soft solder having a melting point of 120-300C.

8. The method of claim 7 in which the solder layer is applied by printing a thick film solder paste onto the solder paste area and drying the paste to remove the organic solvent therefrom.

9. The method of claim 7 in which the solder layer is applied by dipping the solder pad area in a molten solder bath to form a solder coating, removing the solder pad area from the molten solder bath and cooling the applied solder coating.

10. The method of claim 7 in which the glass in the thick film dielectric layer is crystallizable under the firing conditions.

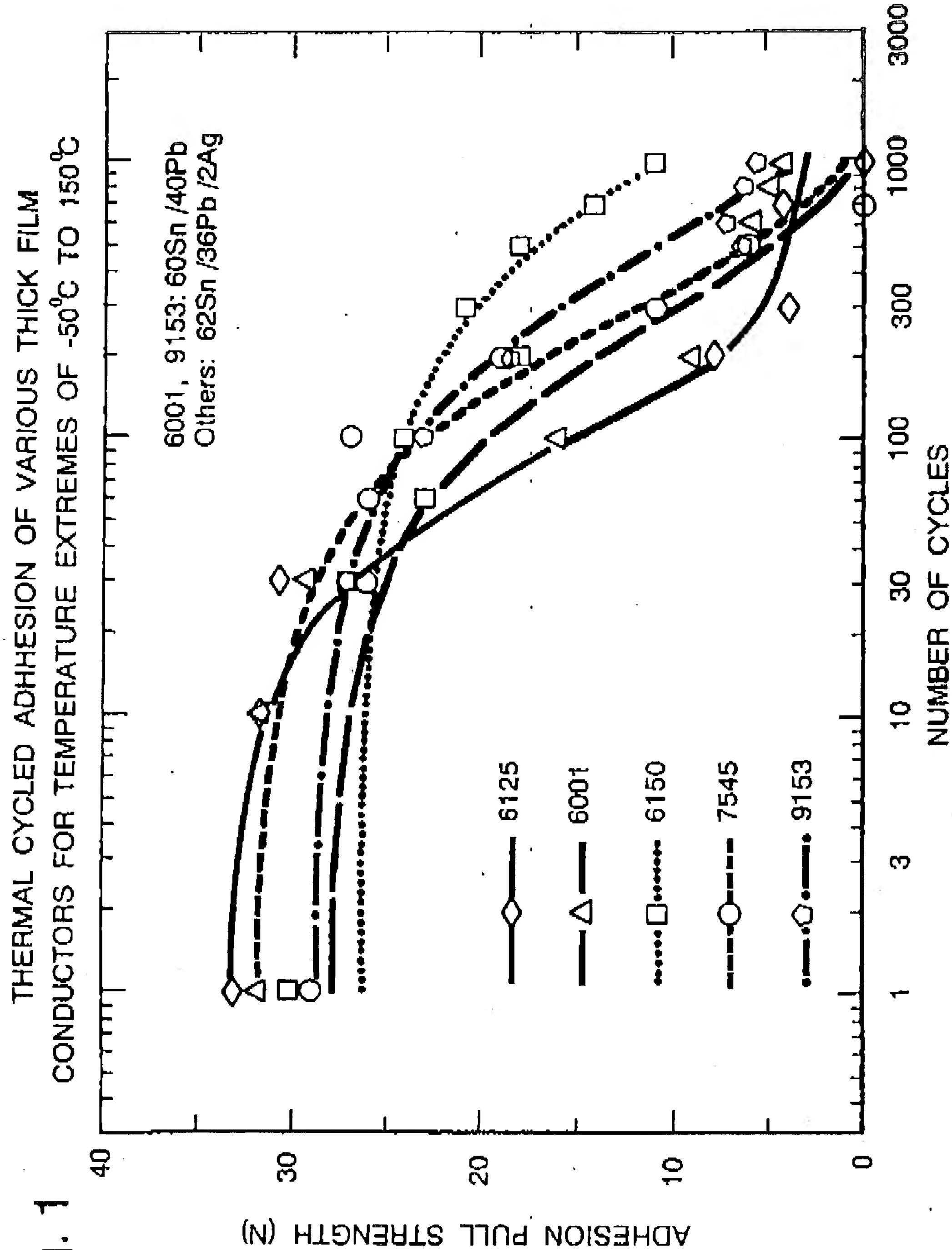
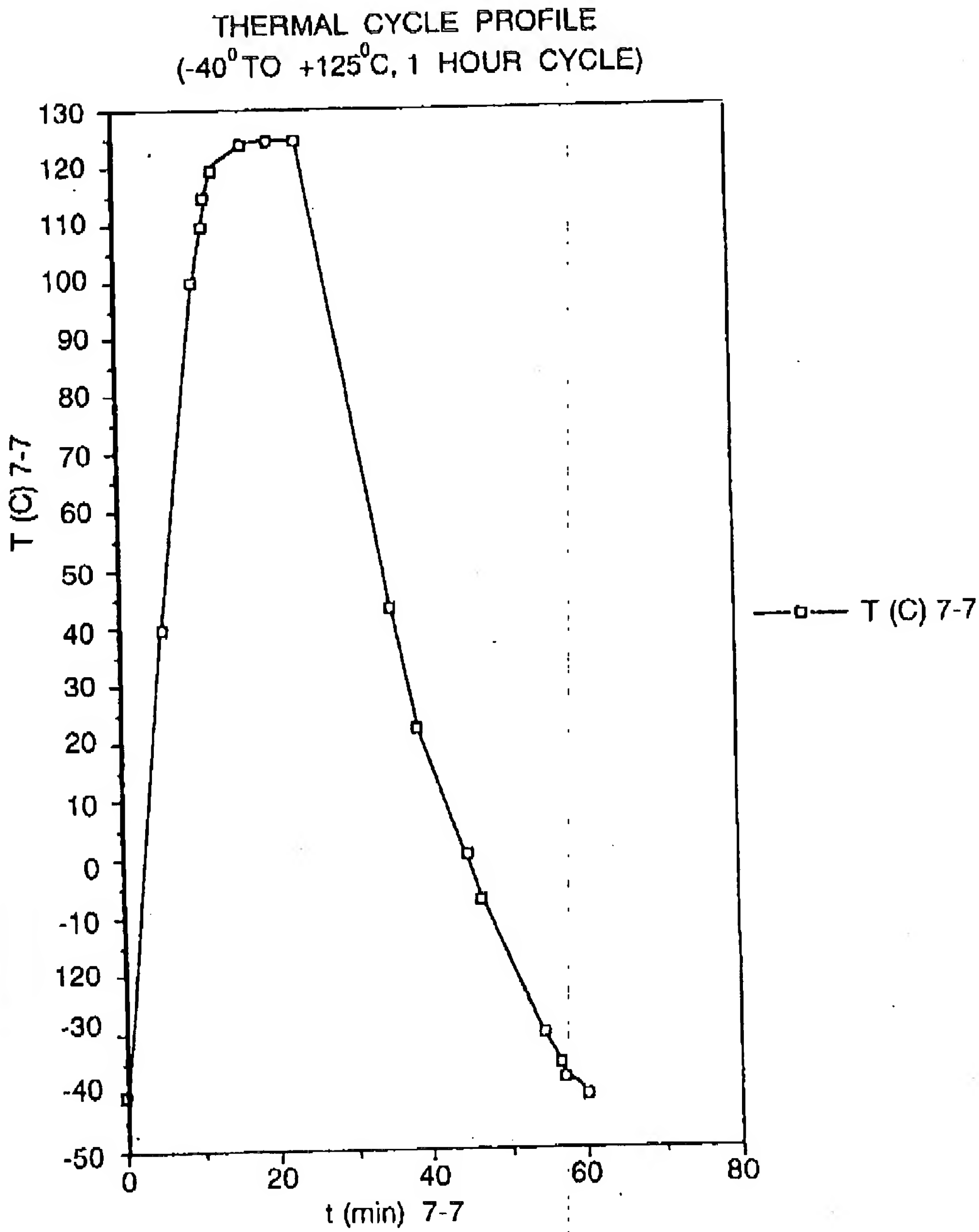

THERMAL CYCLED ADHHESION OF VARIOUS THICK FILM
CONDUCTORS FOR TEMPERATURE EXTREMES OF -50°C TO 150°C
6001, 9153: 60Sn /40Pb
Others: 62Sn /36Pb /2Ag
6125
6001
6150
7545
9153
ADHESION PULL STRENGTH (N)
40
30
20
10
0
1
3
10
30
100
300
1000
3000
NUMBER OF CYCLES

Fig. 1

Fig. 2a


THERMAL CYCLE PROFILE
(-40°TO +125°C, 1 HOUR CYCLE)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
120
-30
-40
-50
T (C) 7-7
0
20
40
60
80
t (min) 7-7
T (C) 7-7

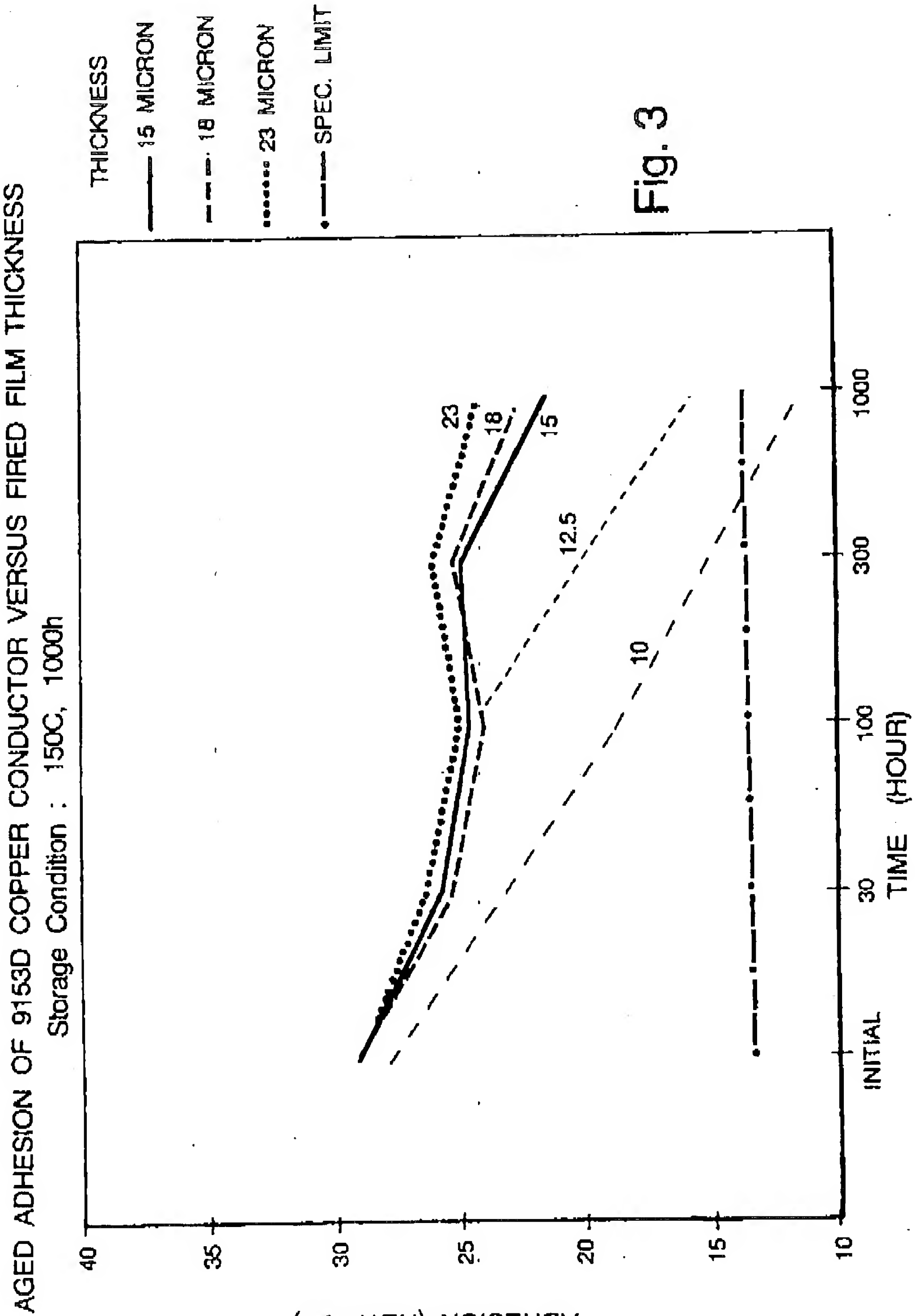

AGED ADHESION OF 9153D COPPER CONDUCTOR VERSUS FIRED FILM THICKNESS
Storage Condition : 150C, 1000h
THICKNESS
15 MICRON
18 MICRON
23 MICRON
SPEC. LIMIT
23
18
15
12.5
10
ADHESION (NEWTON)
40
35
30
25
20
15
10
INITIAL
30
100
300
1000
TIME (HOUR)

Fig. 3

Fig. 4

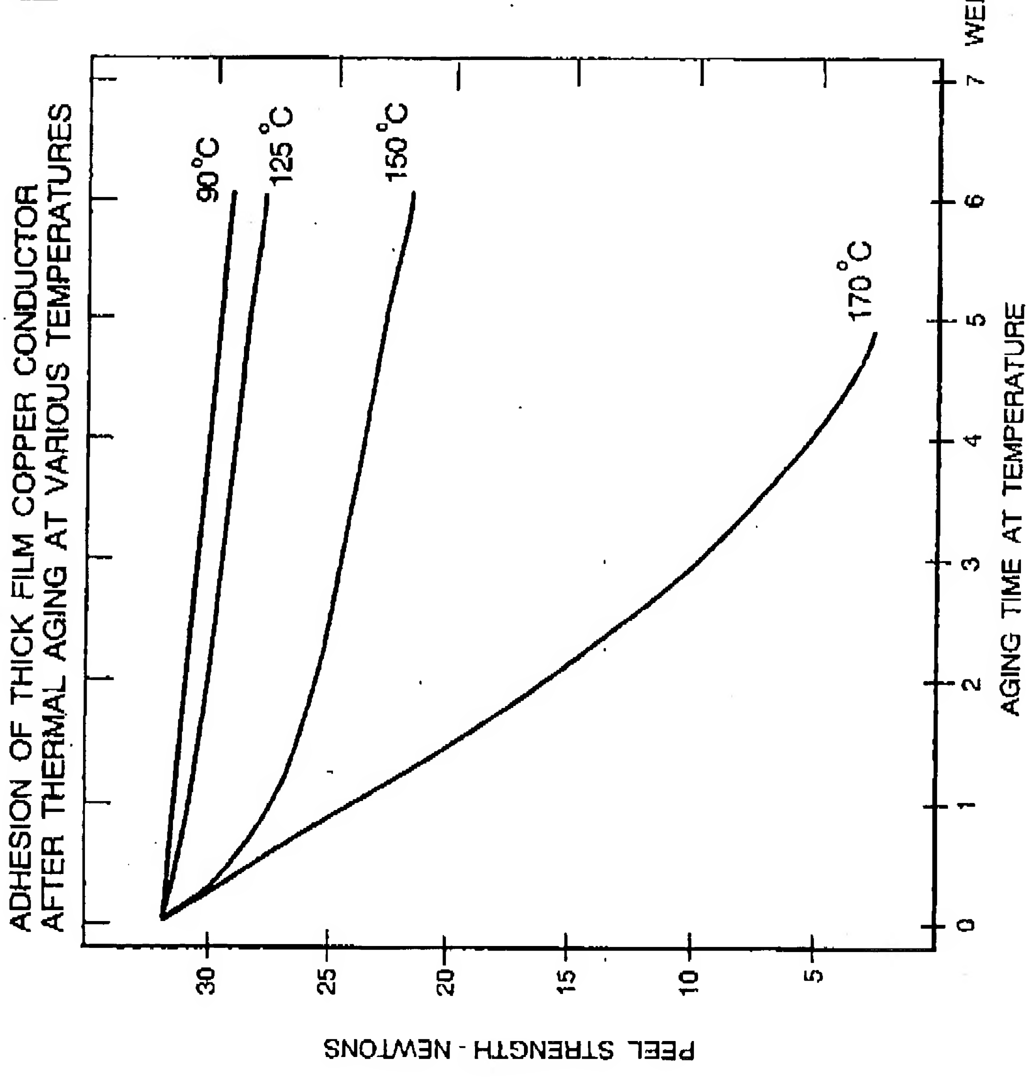

ADHESION OF THICK FILM COPPER CONDUCTOR
AFTER THERMAL AGING AT VARIOUS TEMPERATURES
90 °C
125 °C
150 °C
170 °C
PEEL STRENGTH - NEWTONS
30
25
20
15
10
5
0
1
2
3
4
5
6
7
WEEKS
AGING TIME AT TEMPERATURE

Fig. 5a

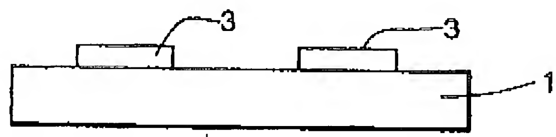


Fig. 5b

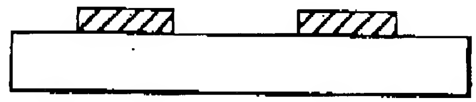


Fig. 5c

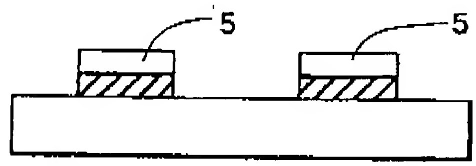


Fig. 5d

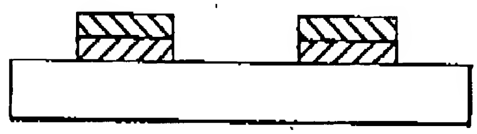
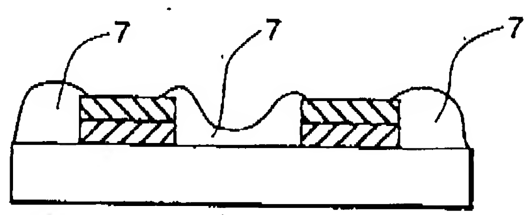


Fig. 5e



Fig, 5f

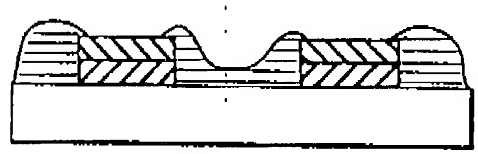


Fig. 5g

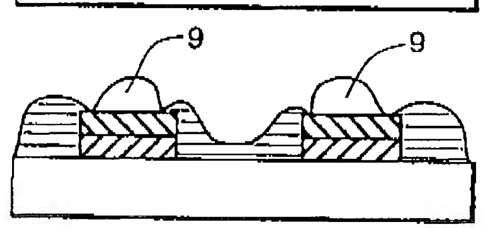


Fig. 6

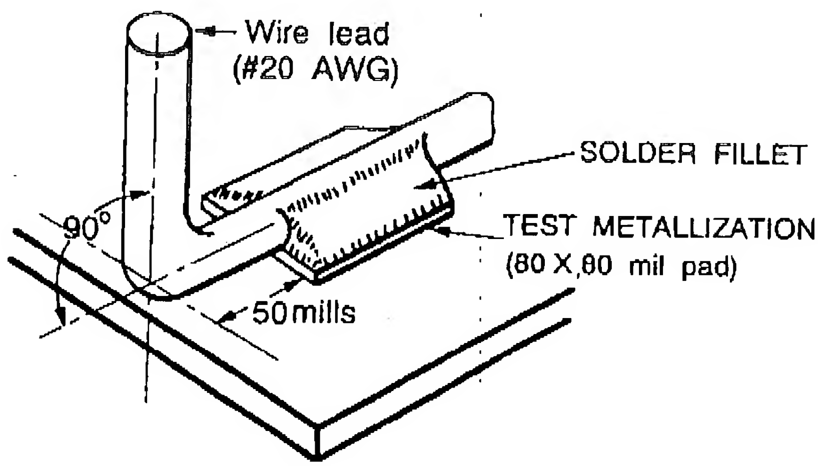


Fig. 7a

STANDARD PEEL TEST

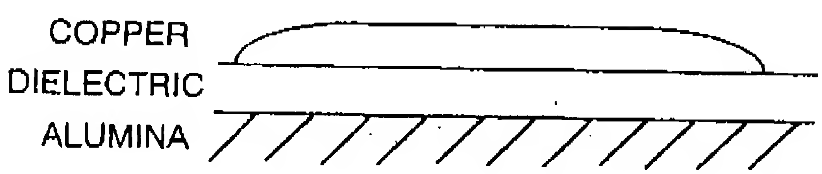


Fig. 7b

MODIFIED PEEL TEST